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A brief overview on radon measurements in drinking water

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ABSTRACT

The aim of this paper is to present information about currently used standard and routine methods for radon analysis in drinking waters. An overview is given about the current situation and the performance of different measurement methods based on literature data. The following parameters are compared and discussed: initial sample volume and sample preparation, detection systems, minimum detectable activity, counting efficiency, interferences, measurement uncertainty, sample capacity and overall turnaround time. Moreover, the parametric levels for radon in drinking water from the different legislations and directives/guidelines on radon are presented.

1. Introduction

On the basis of Articles 35–36 of the EURATOM Treaty (EURATOM, 2010) monitoring and reporting of environmental radioactivity is an obligation for the EU Member States. To check the quality and comparability of these measurement results the Institute for Reference Materials and Measurements (JRC-IRMM/JRC-Geel[1]) is requested by the EC DG ENER to organize interlaboratory comparisons (ILCs). In an upcoming ILC, the focus is on one of the most widespread monitoring methods, radon activity measurement in drinking water samples. In this context this paper gives a brief overview on the current situation and the performance of different radon measurement methods. This paper deals solely with radon (^{222}Rn) and not other more short-lived radon isotopes, like thoron (^{220}Rn) and actinon (^{219}Rn).

Surface and underground waters contain radionuclides as natural components in various concentrations depending on their origin. Radon is released into waters as a result of natural processes like decay of its parent nuclide ^{226}Ra and predominantly dissolution from the surrounding geological environment (rocks, soils) as discussed by (Moreno et al., 2014; Fonollosa et al., 2016). Radon in water may also origin from dissolution of airborne radon into water and other higher radon bearing water in-flows in the catchment area.

Radon solubility in water is relatively low, 0.01 mol kg^{-1} bar^{-1} at 293 K (Lerman, 1979). Solubility is commonly expressed by the partitioning coefficient (L) of ^{222}Rn between pure solvent and air (Clever, 1979; Schubert et al., 2007). The partitioning coefficient of ^{222}Rn in water is approximately 0.23–0.25 at 293 K. Radon affinity towards organic solvents and oils is higher, for example L ≅ 6 for ethanol. This behaviour can be used during the different analytical approaches where phase transfer is needed. The higher the carbon chain length the higher the radon solubility is. Despite the relatively low solubility of radon in water, its activity concentration in waters can be some orders of magnitude higher than that of other natural radionuclides (Fonollosa et al., 2016).

The relatively low cost and simplicity of many radon measurement techniques has made them common to apply in many laboratories. Numerous reliable radon measurement devices are available on the market with reasonably low detection limits, affordable price and simple operation. Furthermore, sample preparation for the water radon analysis is usually simple, rapid and does not need extensive chemical manipulations. This gives an advantage of much shorter turnaround time than other radioanalytical techniques involving radiochemical manipulations. In certain cases result can be delivered even within an hour

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[1] As of 1 July 2016 JRC-IRMM will change its name to JRC-Geel.

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(Todorovic et al., 2012; Lucchetti et al., 2016).

Water intended for drinking purposes has to be analysed for its radon content according to the new EURATOM Drinking Water Directive referred as E-DWD (EURATOM, 2013). Article 8 of the E-DWD stipulates the transposition by 28 November 2015.

Furthermore, this overview aims to contribute 1) finding reliable methods to determine reference values for radon in water samples and; 2) evaluating suitable radon measurements to support work in MS laboratories.

2. Radon in water: regulations and examples

To protect the health of citizens from radon in drinking water, different radon levels are introduced. For waters intended for human consumption the E-DWD establishes parametric values, WHO (WHO, 2008) uses guidance level while in the United States maximum contaminant levels are introduced.

Guidance levels and parametric values should not be regarded as limit or reference values as explained in the E-DWD and WHO publications. The country concerned establishes guidance levels and parametric values on the basis whether that value poses a risk to human health from a radiation protection point of view or not (i.e. if further remediation action is needed or not).

The guidance and parametric levels were reviewed for all MS and are summarized in Table 1. For waters intended for human consumption in the European Union countries guidance and parametric levels are in accordance with the E-DWD, i.e. between 100 and 1000 Bq L^{-1}. It has to be noted that mineral waters are still exempted from this directive despite their regular/preferred consumption. In the United States, two different levels are given for the maximum contaminant level (US-EPA, 1999). Exceeding the highest alternative maximum contaminant level might result in elevated health risks from indoor radon (i.e. radon escaping from water and into the indoor air) so mitigation is needed in the places concerned. The higher alternative maximum contaminant level could contribute approximately one tenth (14.8 Bq m^{-3}) of the total indoor radon which is equivalent to the average outdoors radon concentration in the US (Bartram, 2015). The World Health Organization set the guidance level to 100 Bq L^{-1} in the third edition of the WHO drinking water guidelines (WHO, 2008). However, in the current publication of the drinking water guidelines radon guidance level is missing and no other concrete guidance level is given (WHO, 2011). A selection of international radon guidance and parametric values for drinking waters are presented in Table 1.

Examples of radon concentration in different water sources including extreme high values are presented in Table 2.

Radon activity concentrations are highly variable not only among the different water types but even within the same type. This can be mainly explained by their origin, lithology of the aquifer host rock and the different processes on their way to the consumer (e.g. degassing, dilution, decay). Where drinking water has shorter way and time between the water source and consumer the reduction in radon activity concentration is lower. In general the consumption of water with respect to radon can be considered safe, since the typical radon concentrations of waters fall below the corresponding international and European directives, recommendations. However, there are waters with some extreme values above the parametric and guidance levels so monitoring will remain important. The applied radon measurement techniques should be capable of measuring radon activities with confidence and accuracy in activity concentrations from <1 and up to several thousands of Bq L^{-1}. According to radon activity concentration studies, the majority of the studied drinking and surface waters meet the directives and regulations therefore, no elevated radon risk is present due to water consumption. Those findings are mainly due to the fact that these waters either undergo water treatment (de-gassing) where radon is removed from the waters together with other dissolved gases like methane. Or simply that radon has lower chance to accumulate and higher chance to escape as it happens in the case of surface waters.

The situation is different in case of ground waters, since they are in contact with geological formations rich in uranium and sometimes in a closed or nearly closed system where radon can accumulate and reach activity concentration of several kBq L^{-1}. Waters tend to have higher radon concentration in vulcanite areas and the vicinity of tectonic faults (Fonollosa et al., 2016; Popit and Vaupotič, 2002).

3. Standard water radon measurement methods

There are international standards dedicated to water radon measurements like ISO 13164-3:2013, ISO 13164-4:2015 and ASTM D5072-09 (2016). Besides the technical part, they describe the principles of the methods, some of the sampling issues and approaches, transportation and storage conditions. It is not the aim of this paper to present the standards in detail but to highlight the applicability and pitfalls of these proposed methods to further improve the measurement accuracy.

The major international standards include the following:

a) ISO 13164-3:2013: Water quality - Radon-222- Part 1–3.
   Part 1: General principles
   Part 2: Test method using gamma-ray spectrometry.
   Part 3: Test method using emanometry
b) ISO 13164-4:2015: Water quality Radon-222 - Part 4.
   Test method using two-phase liquid scintillation counting.
c) ASTM D5072-09 (2016) Standard Test Method for Radon in Drinking Water based on LSC.

3.1. Methods

In principle there are three different water radon measurement approaches. The first one uses gamma-ray spectrometry, the

Table 1
International radon guidance and parametric values in drinking water.

Directive/recommendation	Activity concentration (Bq L^{-1})	Reference
EURATOM DWD (E-DWD)	100–1000[a]	EURATOM, 2013
24 EU Member States[b]	100	MS National law
Ireland, Portugal, Spain	500	MS National law
Finland	1000	MS National law
WHO guidance level	100	WHO, 2008
US-EPA maximum contaminant level	~11.1	US-EPA, 1999
US-EPA alternative higher maximum contaminant level	148	

[a] >1000 Bq L^{-1} remedial action without further consideration is justified in all EU countries.
[b] Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, France, Germany, Greece, Hungary, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Romania, Slovakia, Slovenia, Sweden, United Kingdom.

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Table 2
Examples of radon concentration ranges in different water sources.

Water type	^{222}Rn activity concentration (Bq L^{-1})	Country, region	Geology	References
Drinking water	<3	Serbia/Novi Sad		Todorovic et al., 2012
	0.3–24	Cyprus and Greece (Attica-Crete)	Not detailed	Nikolopoulos and Louizi, 2008
	1.46–644	Austria	granite bedrock	Wallner and Steininger, 2007
	<1.3–1800	Germany		Beyermann et al., 2010
	1.9–112.77	Portugal	tap	Lopes et al., 2005
	0.19–71.1	UK	tap	Henshaw et al., 1993
Surface water	<1	Slovenia		ISO 13164-3, 2013
	5.4			Kobal et al., 1990
Groundwater	1–1000	Spain, La Garrotxa region		ISO 13164-3, 2013
	0.2–26		volcanic	Moreno et al., 2014
	3043	Poland, the Sudety Mountains	Volcanic (e.g. crystalline rocks)	Przylibski et al., 2014
	3800	Finland	Soil (no detail)	Salonen, 1988
	1220	Germany, east Bavaria	granite, gneiss	Trautmannsheimer et al., 2002
	17–3856	Portugal, Nisa	Granites, sediments	Pereira et al., 2015
	5.8–36.6	UK, Northern Ireland	Sherwood Sandstone Aquifer	Gibbons and Kalin, 1997
Spring and non-bottled mineral waters	1.4–105	Spain, South Catalonia,	vulcanic (granite) and sedimentary rocks (e.g. limestone, sandstone)	Fonollosa et al., 2016
	2.11–120	Hungary, Balaton Highland, South Transdanubia and The South Great Plain	Sedimentary rocks	Somlai et al., 2007
	Mineral water 0.91–1463	Serbia	various	Todorovic et al., 2012
	1595	Bulgaria, Momin prohod		Pressyanov et al., 2007
	1.4–43.7	Lithuania	crystalline and sediment rocks	Ladygiene et al., 1999
	1.5–181	Italy, Padua, Euganean Thermal District	volcanic rocks	Cantaluppi et al., 2014
	1029	Spain, Galicia	granitic and slate rocks	Llerena et al., 2013
Well water	10–300	Norway		ISO 13164-3, 2013
	32000		Not detailed	Strand et al., 1998
	4–63560	Sweden, Stockholm County	various, crystalline bedrock	Skeppström and Olofsson, 2006
	47–1600	Belgium, Visé		Bourgoignie et al., 1982
	77000	Finland,	mainly granitic bedrock	Salonen, 1988

second emanometry and the third approach is based on liquid scintillation counting. The methods cover a wide range of techniques from simple, cheap but straightforward ones to more sophisticated and expensive detection techniques. For these reasons, radon analysis is available in many more laboratories than some other types of nuclide specific techniques. To get reliable and comparable results, it is advisable to follow one of the standard methods.

It is worth noticing that WHO does not suggest any preferred approach in their drinking water guide (WHO, 2011).

The E-DWD allows Member States to use various screening strategies to indicate the presence of radioactivity in water intended for human consumption but these methods have to be reliable. There are minimum requirements in the E-DWD regarding detection limit and sampling frequency from drinking water supplies. The chosen radon measurement technique has to be capable of measuring activity concentrations with the following limit of detection: The limit of detection for radon is 10% of its parametric value of 100 Bq/L, which is 10 Bq/L.

The annual sampling frequency and number of samples should be defined by Member states but they depend on water volume distributed or produced each day within a supply zone. The E-DWD adds that the number of samples should be distributed equally in time and location as much as possible.

The measurement techniques could be grouped depending on some key aspects, for example application of phase transfer, analysis location, detection systems. The easiest technique is by direct measurement by using gamma-ray spectrometry, without any phase transfer. When phase transfer is involved, ^{222}Rn is transferred from the aqueous phase to another phase. Generally emanometry is used to transfer radon from liquid to gas phase. When liquid scintillation counting is to be used, the target destination matrix is an organic phase. One can also choose to adsorb radon on solid porous surfaces, like activated charcoal, which enables radon to be measured by gamma-ray spectrometry.

It is possible to perform the measurements in-situ using light portable devices. Measurements in a laboratory require careful sampling and then transport under well-defined conditions. The decision on the analysis location depends on many conditions, such as the urgency of the analysis, the available instrumentations, the desired accuracy and the expected radon activity levels. Due to the short ^{222}Rn half-life, 3.8232 (8) days (Bè et al., 2008), decay correction must be considered when measurement starts or possible with delay after sampling and for methods where long measurement times are needed. Samples with low radon activity concentration should be measured in situ or in laboratory but in a short time after sample collection (e.g. within one ^{222}Rn half-life).

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3.1.1. Gamma-ray spectrometry

In gamma-ray spectrometry, the ^{222}Rn activity concentration is derived from the measurement of its daughter products, ^{214}Bi and ^{214}Pb. As the radon-daughters are short-lived, the secular equilibrium is established within 3 h. However, if ^{226}Ra is present in the sample, there is production of ^{222}Rn and it becomes necessary to perform a second measurement after secular equilibrium has been established between ^{226}Ra and ^{222}Rn. Since the ^{222}Rn half-life is almost 4 days one need to wait a significant period of time (preferably 10 half-life) for this correction to be applied, which introduces severe complication. Solid state scintillation detector or high purity germanium (HPGe) detectors are the most commonly used gamma-ray detectors. However, due to their poor resolution solid state detectors based on NaI are mostly used for screening, while HPGe detectors are better suited for qualitative and quantitative analysis.

There are other conditions that can influence the results as well. The sample density and homogeneity are influenced by the water temperature, suspended materials and air bubbles, all of which affect the detection efficiency.

If the ^{226}Ra content in the sample is high then the measurements should be repeated after ten ^{222}Rn half-lives (38 days), with the consequence that analytical results are significantly delayed. The measurement results are, furthermore, influenced by radon (of outdoors and building material origin) in the laboratory air which is known to vary significantly showing daily or seasonal variations in many laboratories especially without air exchange systems. To overcome this, radon-free inert gas can be used to purge the immediate surroundings of the detector and sample as described in the second part of the ISO 13164 standard (ISO 13164-3, 2013).

3.1.2. Emanometry

Emanometry is based on sample degassing followed by alpha particle detection by various detection systems. When a water sample is degassed, ^{222}Rn is transferred to a measurement cell either by an inert gas flow or air circulation or vacuum. Several detection techniques can be applied to determine radon activity concentration in the gas phase including scintillation cells like Lucas cell, semiconductor silicon detector and ionization chamber.

The technique is sensitive to the water temperature as it can influence the level of degassing during transport (ISO 13164-3, 2013). Detector contamination has to be checked to make sure that low level radon analysis can be performed and no build-up of longer living daughter products (e.g. ^{210}Po) has occurred. Some water samples can contain high levels of ^{220}Rn (thoron) which can be transferred to the detection system as well.

One degassing approach is to place water sample in a degassing cell and introduce radon free air or inert gas in a closed system. In this way, radon is purged from the sample and with a help of a pump carried to the counting cell or detector. Radon activity concentration in the air will be measured and the initial concentration in water can be derived from this measurement.

Another degassing approach is to inject a small aliquot of sample directly into a partially vacuumed scintillation cell with a syringe. Due to vacuum, radon is released from the water sample then the pressure is adjusted to normal ambient pressure by introducing radon free air or inert gas. In three hours after injection the scintillation cell is ready for counting.

3.1.3. Liquid scintillation counting (LSC)

The principle of the radon measurement by LSC is based on the extraction of ^{222}Rn from the water to the immiscible scintillation cocktail. First the necessary volume of scintillation cocktail is transferred into an LSC vial. Sample is taken well below the surface and introduced slowly into the LSC vial below the LSC cocktail by a gas tight syringe. Then the vial is air tight closed shaken well and stored for three hours in a dark room with stable temperature then the sample can be counted.

^{222}Rn and its short-lived progenies are measured by selecting either the alpha + beta or the alpha-only mode of the LS spectrometer. In order to obtain optimal counting statistics, a water sample volume between 500 and 900 mL is suggested for LSC analysis with the use of 20-mL scintillation vials (Schubert et al., 2014).

In LSC the discrimination setting is crucial as it can easily lead to erroneous results. Photo and chemiluminescence may also occur, but the latter mainly in case of single phase cocktails. Photoluminescence can be avoided by sufficient storage time of a few hours in a dark place before starting the measurement.

Another source of error could be the calibration. Usually, a^{226}Ra standard or reference solution is used for this purpose with the selected liquid scintillation cocktail. However, if an old (>5 years) ^{226}Ra calibration solution is used then ^{210}Pb and its progenies co-extract with ^{222}Rn and results in incorrect efficiency calibration (Salonen, 2010). This contribution using mineral oil based cocktail amounts to about 4% for a 5-year old and already 12% for a 20-year old calibration solution. The degree of extraction of the ^{222}Rn progenies and therefore the calibration errors depend on the scintillation cocktail and it is suggested that the cocktails should be studied in case by case.

3.2. Main features of the detection systems

A comparison of the various detection systems and approaches used for the determination of radon in water are shown in Table 3, together with a summary of their main features. These data are based on literature data and the ISO 13164 standard (ISO 13164-3, 2013; ISO 13164-4, 2015).

One of the most important performance indicators of a method is its detection limit. All of the detection systems mentioned here comply with the detection limit requirement derived from the E-DWD. They all can measure radon activity concentration down to 10 Bq L^{-1} as calculated for the lowest detection limit in case of 100 Bq L^{-1} radon parametric level. The typical measurement uncertainties are usually below 20% (coverage factor, $k = 1$). However, the initial sample volume varies in a wide range from 10 mL up to few L depending on the method used and the required sample preparation. In general, there is no consensus on the initial sample volume for most of the methods, only few studies make an attempt to optimize the initial sample volume, for example, for LSC analysis (Schubert et al., 2014). For in-situ analysis it is suitable to use almost all types of detection systems, maybe except gamma-ray spectrometry. Portable gamma-ray spectrometers exist but they are mainly equipped with solid state scintillation detectors. According to the ISO 13164 standard they can be used for screening as only semi-quantitative information can be derived.

In a field laboratory with high sample load, an additional important parameter is the turnaround time of an analysis method. In this case, the turnaround time is sufficiently short, in the range of few hours, unless correction for ^{226}Ra is necessary. Furthermore, there are techniques which provide measurement data even quicker, within minutes after sampling which is a real advantage. There are even detector systems capable of performing continuous radon water measurement using mainly ionization chamber or silicone detectors (Papastefanou, 2002). The time between sampling and analysis reporting should be less than 48 h in all cases.

4. Sample manipulations and storage affecting measurement results

It was already pointed out that sampling, transport and storage have significant impact on the measurement results (Gruber et al.,

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Table 3
Overview of water radon measurement techniques.

Detection system	Counting efficiency	Achievable lowest detection limit (Bq L^{-1})[a]	Typical measurement uncertainty ($k = 1$)	Typical sample volume (L)	Sample treatment	Turnaround time (hour)	In-situ measurement possible
Gamma-ray spectrometry	1.5%[c]	10	5–15%	0.1–2	No	4–13	No
Ionization chamber		0.3	5–12%	0.05–0.2	Degassing	≤1	Yes
LSC	280–300%[b]	0.05–1	≅ 10%	0.01–2	Depends on cocktail	3–8	Yes
Scintillation/ Lucas cells	15–90%	0.3–1	<10%	0.05–1	Degassing	1–3	Yes
Silicon detector		0.04–0.4	5–12%	0.1–0.4 1–2	Degassing Permeation	≤1 Few hours	Yes Yes

[a] E-DWD detection limit: 10% of the parametric value of 100 Bq/l, 10 Bq L^{-1}.
[b] Including ^{222}Rn, ^{218}Po, ^{214}Po.
[c] Absolute efficiency simulation for a 1 L sample at 609 keV peak.

2009). The very first and probably the most important manipulation is sampling, where a considerable fraction of radon can be lost.

Besides sampling, storage is another important phase in radon analysis. Storage conditions, storage time and container material strongly influence the measurement results if analysis is performed days later after the sample is collected.

Different container materials were studied and it was found that polyethylene terephthalate (PET) and polylactic biopolymer (PLBP) are better suitable materials than polyethylenes (HD/LDPE) (Leaney and Herczeg, 2006; Lucchetti et al., 2016). After four days of storage in PET/PLBP and PE containers 2% and 15–27% radon loss was observed, respectively (Lucchetti et al., 2016). Below 5% radon loss was found from glass bottles after 5 days (Vesterbacka et al., 2010).

When transport is needed then water temperature should be kept stable as it can influence the level of degassing and eventually radon loss during transport. Low temperature, preferably lower than the temperature at the time of sampling but above 0 °C to avoid freezing, helps preserving radon in the sample. Contact between water sample and air should be avoided, especially if a ^{222}Rn concentration below 10 Bq L^{-1} is expected in the sample. When degassing is applied then the radon transfer efficiency is assumed to be close to 100% but it is suggested to be determined for each sample.

There are general considerations regarding sample handling, manipulation and storage which have to be taken into account.

One of the most important general considerations during sampling is to avoid any contact between the sample and the environmental air. For ensuring this, gas tightness during sampling and transport is needed. The container should be made from preferably glass or non-porous material which meets gas sampling standards. If gamma-ray spectrometry is used immediately after sampling then the container should be made of non-conductive material to avoid absorbing radon daughters from the environment. Furthermore, in a sample container with empty space, ^{222}Rn gas occupies the empty space. This changes the counting geometry for ^{222}Rn and its progenies therefore the counting efficiency. This can be avoided by filling the empty space of the container as much as possible so that ^{222}Rn stays in the sample itself.

There are different sampling strategies for samples depending on water sources and if it is running water or stagnant water as briefly introduced in the next paragraphs. The sampling procedures can be found in more details in the corresponding ISO standards (ISO 5667-1, 2006; ISO 5667-3, 2012; ISO 13164-3, 2013).

When sample is taken from stagnant/still water or flowing water then the container should be fully immersed in the water body and closed under water when it is completely full and no air bubbles present. In case of flowing water the mouth of the container should point at the direction from which the water is flowing.

Before sampling from tap, faucet or spring the water should be allowed to run for few minutes to let water from the possibly stagnant pipe section flow. Furthermore, the aerators from taps should be removed if present to avoid air bubbles in the sampling container. During sampling the water flow should be adjusted to avoid turbulence. The container should be filled with the sample carefully; water should flow on the inner wall of the container until it is completely filled and no air bubbles present. Then, the container can be closed air-tight with the container cap. If sample is taken with a syringe then it has to be done by a gas-tight syringe.

5. Uncertainty contributions and method validation

As far as the uncertainty contributions are concerned they may vary in a wide range even in normal conditions (from <1% up to the range of 100% in some exceptional cases). Laboratories should have the capability to identify the uncertainty sources and quantify them to give a sound and realistic uncertainty budget. Usually the following elements are the main uncertainty contributors listed in the order of significance: counting statistics, instrument calibration (counting efficiency), transfer efficiency where de-gassing is involved, efficiency calibration sources and, to lesser extent, radon decay calculation to a reference date. Here we have to note that sampling and sample preparation are errors and not uncertainties but eventually they influence the end result. The summary on the uncertainty sources are given in Table 4.

Uncertainties on the counting time, pressure, temperature are stated to be neglected (ISO 13164).

The ISO 13164-1:2013 mentions that method verification is an essential part of the laboratory work and has to be done on a regular basis by analysing reference materials. Furthermore, method accuracy and repeatability should be checked too. This ISO standard also stresses the importance of participating in interlaboratory comparisons or proficiency tests.

6. Instrument calibration

To improve the situation of the available calibration options there were some international efforts to make reliable primary radon standards and further develop secondary standards (De Felice, 2007). Besides the common ^{226}Ra calibration approach and its pitfalls, radon-in-water standard source is already used for method calibration in practice (Forte et al., 2007).

6.1. Gamma-ray spectrometry

The calibration of the high purity germanium detector can be

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Table 4
Summary of the uncertainty sources for gamma-ray spectrometry, emanometry and liquid scintillation counting.

Uncertainty sources	Gamma-ray spectrometry	Emanometry	Liquid scintillation counting
Counting statistics	+	+	+
Counting efficiency	+	+	+
Radon transfer	n.a.	+	n.a.
Activity of the calibration source or solution	+	+	+
Calibration factor	n.a.	+	n.a.
Sample volume	+	+	n.a.
Counting cell volume (scintillation cell or ionization chamber)	n.a.	+	n.a.
Radon concentration in the ionization chamber before sample injection	n.a.	+	n.a.
Uncertainty on ^{222}Rn half-life	+	+	+
Spectrum analysis (coincidence correction/emission probability)	+	n.a.	n.a.
Total efficiency	n.a.	n.a.	+
Weighing (sample, standard solution)	n.a.	n.a.	+

+: applicable; n.a.: not applicable.

performed either experimentally or using Monte Carlo simulation.

The ^{226}Ra calibration solution with an accurately known activity is placed in a gas tight container. After achieving secular equilibrium between ^{226}Ra and ^{222}Rn gamma spectrometry analysis is performed. The counting efficiencies are determined at the energy regions of two of ^{222}Rn short lived decay products, ^{214}Pb and ^{214}Bi. It has to be noted that for the counting efficiency calculations at certain energy the gamma-ray emission probabilities have to be taken into account. Blank sample is prepared by weighing the same mass of degassed distilled or deionized water into a gas tight container and measured in the same way as the calibration standard.

The Monte Carlo simulation needs many input parameters such as the measurement geometry, detector source distance, sample holder material and wall thickness, radioactivity distribution in the calibration sample.

6.2. Emanometry

The alpha counting efficiency of a scintillation cell can be determined by using radon in air calibration chambers with accurately established ^{222}Rn activity concentration. Radon is transferred from the calibration chamber to the previously evacuated scintillation cell. Measurement and calculation can be done by following the routine procedure.

If de-gassing is applied to transfer radon from the aqueous phase to the gas flow, then either the radon transfer efficiency for the degassing time or the time to achieve close to 100% de-gassing efficiency should be determined. Some detectors (e.g. based on ionization chamber) can be calibrated at the national metrology's radon calibration facilities.

6.3. Liquid scintillation counting (LSC)

For preparing calibration sources ^{226}Ra or ^{222}Rn standard solution can be used if available. If ^{222}Rn standard is used then the calibration source can be used already after three hours after its preparation. Only ^{222}Rn is extracted into the organic scintillator but ^{226}Ra stays in the aqueous phase. Therefore, it doesn't influence the counting efficiency calibration. As water and other dissolved materials are not transferred into the scintillation cocktail only ^{222}Rn then quenching correction is not needed.

The calibration procedure is the following. An accurately known mass of standard solution is transferred into a scintillation vial. Then degassed distilled or deionized water is added up to the preliminary defined mass and the scintillation cocktail is added. In case of ^{226}Ra standard the sample should be stored to achieve secular equilibrium between ^{226}Ra and ^{222}Rn. Before starting the LSC counting the counting conditions have to be optimized. Measurements with alpha-beta discrimination or alpha + beta counting mode are also used. The choice might depend on the achievable detection limit which is lower in case of selecting alpha-beta discrimination. The method linearity should be checked covering the working range. Blank samples are prepared the same way as the calibration sources using the same quantity of degassed distilled or deionized water but the difference is that radioactive standard solution is not added.

7. Conclusions

A literature overview was given on the most common water radon measurement techniques as a reaction to the E-DWD which includes radon in its scope. The performance of each of the discussed methods seems to be adequate for radon activity measurements in drinking waters. In general the methods are straightforward and capable of providing prompt measurement information about radon levels in water samples. Having noted this it must be emphasized that as ^{222}Rn is an inert gas it can easily escape the measurement volume which makes all methods inherently less robust. A further complication could be the lack of information regarding the state of equilibrium with its mother, ^{226}Ra. These obstacles may be overcome using a second complimentary technique. This may be impractical for routine monitoring but constitute a possibility to realise at regular quality controls. In any case, whichever technique is chosen according to the laboratory or customer demands and sample analysis capabilities, it must be repeatable, validated and preferably standardized.

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